Lorenzo J. Curtis

Semiempirical formulations of line strengths using singlet-triplet mixing angles

ABSTRACT

Results are presented in which singlet-triplet mixing angles for two valence electron (or hole) isoelectronic sequences are determined from energy level data. These are utilised together with transition moments obtained from other sequences and from LS coupling and hydrogenic formulae to specify E1 and M1 oscillator strengths.

INTRODUCTION

For systems with two out-of-shell electrons, singlet-triplet and L-state mixing within a given configuration manifests itself in the energy splittings, line strengths, and g-factors of the constituent levels. In intermediate coupling, the wave functions of levels with common J are an admixture of LS basis states not subject to the ΔL and ΔS selection rules that restrict the constituent amplitudes. In *ab initio* calculations this is implicitly included in the wave function. It is also possible to empirically determine the mixing amplitudes explicitly from energy level data, to combine these with transition moments obtained by semiempirical methods, and thereby to specify line strengths (and g-factors) for two-electron systems.

MIXING ANGLES

The $nsn'\ell$, $nsn'p^5$, np^2 and np^4 configurations are particularly apt examples, since they contain no more than two levels of the same J, so that intermediate coupling connects the LS basis states only pairwise. Specification is given by two-by-two off-diagonal matrices M and diagonalisation is achieved by a basis transformation $T^{-1} M T$, where

$$T = \begin{pmatrix} \cos\vartheta_J & \sin\vartheta_J \\ -\sin\vartheta_J & \cos\vartheta_J \end{pmatrix}$$

Here ϑ_J is the mixing angle, given by

$$\sin\vartheta_J = \left[1 + (W_J \pm \sqrt{1 + W_J^2}\,)^2 \right]^{-1/2} .$$

Using Slater energy relationships which relate the levels within a configuration, the quantity W_J can be specified in terms of their J centroid energies ε_J.

For the $nsn'\ell$ configuration, the $J=\ell$ levels are mixed and W_J is given by

$$W_\ell = -\frac{\ell\varepsilon_{\ell+1} - (2\ell+1)\varepsilon_\ell + (\ell+1)\varepsilon_{\ell-1}}{\sqrt{\ell(\ell+1)}\,(\varepsilon_{\ell+1} - \varepsilon_{\ell-1})}$$

For $\ell=1$ this describes both the $nsn'p$ and the $nsn'p^5$ configurations, and the mixing is between the $^3P_1$ and $^1P_1$ levels.

For the np^2 and np^4 configurations there are two mixing angles. For $J=0$, the mixing between the $^3P_0$ and $^1S_0$ is given by

$$W_0 = -\frac{10\,\varepsilon_2 - 21\,\varepsilon_1 + 11\,\varepsilon_0}{4\sqrt{2}\,(5\,\varepsilon_2 - 3\,\varepsilon_1 - 2\,\varepsilon_0)}$$

whereas for $J=2$, the mixing between the $^3P_2$ and ^1D is given by

$$W_2 = -\frac{5\,\varepsilon_2 + 3\,\varepsilon_1 - 8\,\varepsilon_0}{2\sqrt{2}\,(5\,\varepsilon_2 - 3\,\varepsilon_1 - 2\,\varepsilon_0)}$$

LINE STRENGTHS

In terms of these mixing angles, the line strengths for the resonance and intercombination lines in an ns^2-$nsn'p$ or an np^5-$nsn'p^5$ transition is
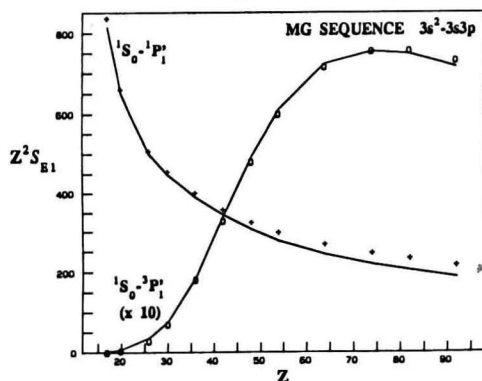
$$S_{E1}(^1S_0, {}^1P_1') = k\cos^2\vartheta_1\,|\langle ns|r|n'p\rangle|^2$$

$$S_{E1}(^1S_0, {}^3P_1') = k\sin^2\vartheta_1\,|\langle ns|r|n'p\rangle|^2$$

where the factor k accounts for the number of equivalent electrons (k=2 for ns^2-$nsn'p$; k=6 for $n'p^6$-$nsn'p^5$).

Fig.1 presents an application to the $3s^2$-

Figure 1

3s3p transition in the Mg sequence, using the transition moments obtained from the Na sequence (Kim & Cheng, 1978), adjusted by an overall factor 1.25. In all figures to follow, solid lines trace semiempirical values and symbols denote *ab initio* calculations (Cheng & Johnson, 1977).

Fig. 2 presents a similar example for the $2p^6-2p^5 3s$ transition in the Ne sequence (Ivanova & Glushkov, 1986), using a fully screened hydrogenlike transition moment, adjusted by an overall factor 0.73. (*Ab initio* values, Biémont & Hansen, 1987.)

Figure 2
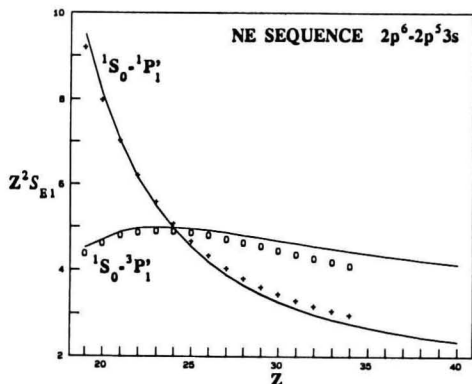
The M1 line strengths within an $nsn'p$ configurations are given by (Curtis, 1989)

$$S_{M1}(^3P'_1, ^3P_0) = 2\cos^2\vartheta_1$$
$$S_{M1}(^3P_2, ^3P'_1) = (5/2)\cos^2\vartheta_1$$
$$S_{M1}(^1P'_1, ^3P_0) = 2\sin^2\vartheta_1$$
$$S_{M1}(^1P'_1, ^3P'_1) = (3/2)\cos^2\vartheta_1\sin^2\vartheta_1$$
$$S_{M1}(^1P'_1, ^3P_2) = (5/2)\sin^2\vartheta_1$$

and for the np^2 and np^4 configurations by

$$S_{M1}(^3P_1, ^3P'_0) = 2\cos^2\vartheta_0$$
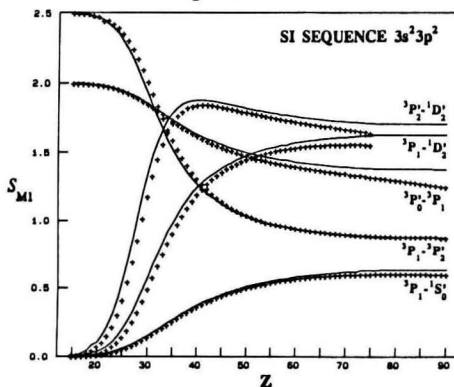$$S_{M1}(^3P'_2, ^3P_1) = (5/2)\cos^2\vartheta_2$$
$$S_{M1}(^1D'_2, ^3P_1) = (5/2)\sin^2\vartheta_2$$
$$S_{M1}(^1D'_2, ^3P_2) = (135/2)\cos^2\vartheta_2\sin^2\vartheta_2$$
$$S_{M1}(^1S'_0, ^3P_1) = 2\sin^2\vartheta_0$$

Fig. 3 displays applications of these formulae to the Si sequence (Huang, 1985).

Figure 3

This semiempirical exposition provides a useful means for comparison of theoretical and experimental results, and characterises and separates intermediate coupling effects.

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AUTHOR'S ADDRESS: Dept. Physics and Astronomy, Univ. of Toledo, Toledo Ohio 43606 USA